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Patentanmeldung Nr. Patent application No. Demande de brevet n°

02358017.8

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Supported polymerisation catalyst

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SUPPORTED POLYMERISATION CATALYST

The present invention relates to supported catalysts suitable for the polymerisation of olefins and in particular to supported metallocene catalysts providing advantages for operation in gas phase processes.

In recent years there have been many advances in the production of polyolefin

- 5 homopolymers and copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally a higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single site in nature.

There have been developed several different families of metallocene complexes.

- 10 In earlier years catalysts based on bis (cyclopentadienyl) metal complexes were developed, examples of which may be found in EP 129368 or EP 206794. More recently complexes having a single or mono cyclopentadienyl ring have been developed. Such complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436. In both of these complexes the metal atom eg. zirconium is in the highest oxidation state.

- 15 Other complexes however have been developed in which the metal atom may be in a reduced oxidation state. Examples of both the bis (cyclopentadienyl) and mono (cyclopentadienyl) complexes have been described in WO 96/04290 and WO 95/00526 respectively.

- 20 The above metallocene complexes are utilised for polymerisation in the presence of a cocatalyst or activator. Typically activators are aluminoxanes, in particular methyl aluminoxane or compounds based on boron compounds. Examples of the latter are borates such as trialkyl-substituted ammonium tetraphenyl- or tetrafluorophenyl-

borates. Catalyst systems incorporating such borate activators are described in EP 561479, EP 418044 and EP 551277.

The above metallocene complexes may be used for the polymerisation of olefins in solution, slurry or gas phase. When used in the gas phase the metallocene complex and/or the activator are suitably supported. Typical supports include inorganic oxides eg. silica or polymeric supports may alternatively be used.

Examples of the preparation of supported metallocene catalysts for the polymerisation of olefins may be found in WO 94/26793, WO 95/07939, WO 96/00245, WO 96/04318, WO 97/02297 and EP 642536.

WO 98/27119 describes supported catalyst components comprising ionic compounds comprising a cation and an anion in which the anion contains at least one substituent comprising a moiety having an active hydrogen. In this disclosure supported metallocene catalysts are exemplified in which the catalyst is prepared by treating the aforementioned ionic compound with an organometallic compound such as triethylaluminium (TEA) followed by subsequent treatment with the support and the metallocene.

Among the organometallic compounds disclosed in WO 98/27119 are aluminoxanes, in particular methyl aluminoxane (MAO) although no further details nor exemplification of such compounds is described.

We have now surprisingly found that the use of aluminoxanes as the organometallic compound has particular advantages relating to the activity profile of the resultant supported metallocene catalysts.

Thus according to the present invention there is provided a method for the preparation of a supported metallocene catalyst system said method comprising the steps of:

- (i) mixing together in a suitable solvent
 - (a) aluminoxane and
 - (b) an ionic activator comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen,
- (ii) addition of the mixture from step (i) to a support material, and
- (iii) addition of a metallocene complex in a suitable solvent.

Suitable solvents for use in the present invention include alkanes eg isohexane or cyclohexane or aromatic solvents eg - toluene.

The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylum cations, oxonium cations, organometallic cations and cationic oxidizing agents.

5 Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

10 The preferred ionic activators are those wherein the cation of the ionic activator comprises a hydrocarbyl substituted ammonium salt and the anion comprises an aryl substituted borate.

Suitable activators of this type are described in WO 98/27119 the relevant portions of which are incorporated herein by reference.

15 Particular preferred activators of this type are alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred activator is bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate.

The preferred aluminoxane is tetraisobutylaluminoxane.

20 The preferred molar ratio of the tetraisobutylaluminoxane to ionic activator is typically 2.

The ratio of aluminium (TiBAO) to boron (activator) is typically 4

According to another aspect of the present invention there is provided a catalyst component comprising the product of

(a) tetraisobutylaluminoxane and

25 (b) an ionic activator comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen,

Suitable support materials include inorganic metal oxides or alternatively polymeric supports may be used.

30 The most preferred support material for use with the supported catalysts according to the process of the present invention is silica. Suitable silicas include Crosfield ES70 and Davison 948 silicas.

The support material may be subjected to a heat treatment and/or chemical

treatment to reduce the water content or the hydroxyl content of the support material. Typically chemical dehydration agents are reactive metal hydrides, aluminium alkyls and halides. Prior to its use the support material may be subjected to treatment at 100°C to 1000°C and preferably at 200 to 850°C in an inert atmosphere under reduced pressure.

The support material may be further combined with an organometallic compound preferably an organoaluminium compound and most preferably a trialkylaluminium compound in a dilute solvent.

A particularly preferred trialkylaluminium compound for use in the present invention is triisobutylaluminium.

The support material is pretreated with the organometallic compound at a temperature of -20°C to 150°C and preferably at 20°C to 100°C.

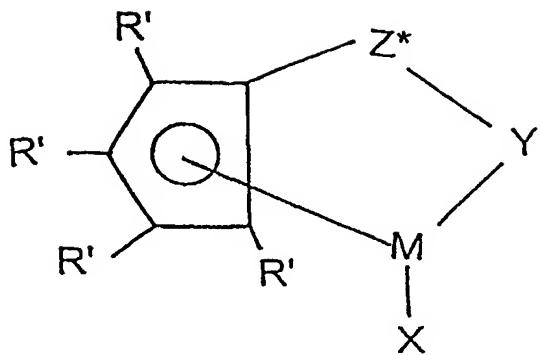
The metallocene complex may comprise for example a traditional bis(cyclopentadienyl) metallocene complex or more preferably a monocyclopentadienyl complex having a 'constrained geometry' configuration.

Bis(cyclopentadienyl) metallocene complexes may be represented by those disclosed in EP 129368 or EP 206794. Such complexes may be unbridged eg. bis(cyclopentadienyl) zirconium dichloride or bridged eg. ethylene bis(indenyl) zirconium dicloride. Other suitable metallocene complexes are those bis(cyclopentadienyl) diene complexes described in WO 96/04290.

Examples of monocyclopentadienyl complexes suitable for use in the present invention are described in EP 416815, EP 418044, EP 420436 and EP 551277.

Particularly suitable monocyclopentadienyl complexes are those disclosed in WO 95/00526 the disclosure of which is incorporated herein by reference.

Preferred metallocene complexes for use in the preparation of the supported catalysts of the present invention may be represented by the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to

- 5 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral η^4 bonded diene group having up to 30 non-hydrogen atoms, which forms a π complex with M;

10 Y is -O-, -S-, -NR*-, -PR*-,

M is titanium or zirconium in the + 2 formal oxidation state;

Z* is SiR*₂, CR*₂, SiR*₂SIR*₂, CR*₂CR*₂, CR*=CR*, CR*₂SIR*₂, or GeR*₂, wherein:

- 15 R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z* (when R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring system.

- Examples of suitable X groups include s-trans- η^4 -1,4-diphenyl-1,3-butadiene, s-
20 trans- η^4 -3-methyl-1,3-pentadiene; s-trans- η^4 -2,4-hexadiene; s-trans- η^4 -1,3-pentadiene; s-trans- η^4 -1,4-ditolyl-1,3-butadiene; s-trans- η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis- η^4 -3-methyl-1,3-pentadiene; s-cis- η^4 -1,4-dibenzyl-1,3-butadiene; s-cis- η^4 -1,3-

pentadiene; s-cis- η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a π -complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire 5 C₅R'₄ group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, terahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula -N(R'')- or -P(R'')- wherein R'' is C₁₋₁₀ hydrocarbyl.

10 Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

Most preferred complexes are those wherein M is titanium.

Most preferred complexes are those wherein M is titanium.

Specific complexes suitable for use in the preparation of the supported catalysts of the present invention are those disclosed in the aforementioned WO 95/00526 and are 15 incorporated herein by reference.

A particularly preferred complex for use in the preparation of the supported catalysts of the present invention is (t-butylamido) (tetramethyl- η^5 -cyclopentadienyl) dimethyl silanetitanium - η^4 -1,3-pentadiene.

In a preferred process according to the present invention, the supported catalyst 20 is prepared by use of a one-pot procedure. This allows for a more efficient procedure as well as having economic benefits.

By one-pot is meant a preparation carried out without the need for washing steps and typically wherein the contact between the support material, ionic activator and metallocene is performed in a single reaction vessel.

25 The one-pot procedure may also incorporate a final precipitation step, using for example the addition of hexane to the mixture resulting from step (iii). In this procedure a slurry or mud of the catalyst is obtained which may be used directly to inject the catalyst into the polymerisation reactor.

The molar ratio of metallocene complex to ionic activator employed in the 30 method of the present invention may be in the range 1:10000 to 100:1. A preferred range is from 1:5000 to 10:1 and most preferred from 1:10 to 10:1.

The supported metallocene catalysts of the present invention are most suitable

for operation in the gas phase. Gas phase processes for the polymerisation of olefins, especially for the homopolymerisation and the copolymerisation of ethylene and α -olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art. Particularly preferred gas phase processes are those operating in a fluidised bed.

- 5 Examples of such processes are described in EP 89691 and EP 699213 the latter being a particularly preferred process for use with the supported catalysts of the present invention.

Particularly preferred polymerisation processes are those comprising the polymerisation of ethylene or the copolymerisation of ethylene and α -olefins having 10 from 3 to 10 carbon atoms.

Thus according to another aspect of the present invention there is provided a process for the polymerisation of ethylene or the copolymerisation of ethylene and α -olefins having from 3 to 10 carbon atoms, said process performed under polymerisation conditions in the present of a supported metallocene catalyst system prepared as 15 hereinbefore described.

The present invention will now be further illustrated with reference to the following examples:

Abbreviations

TEA	triethylaluminium
20 TiBAO	tetraisobutylalumininoxane
TiBA	triisobutylaluminium
Ionic Activator A	[N(H)Me(C ₁₈₋₂₂ H ₃₇₋₄₅) ₂][B(C ₆ F ₅) ₃ (C ₆ H ₄ OH)]
Complex A	(C ₅ Me ₄ SiMe ₂ N ^t Bu)Ti(η ⁴ -1,3-pentadiene)

Example 1

25 Catalyst preparation

To 3g. of Ineos ES70 silica (previously calcined at 500°C for 5 hours under nitrogen, pore volume 1.55 ml/g) was added a solution made with 2.81 ml of a hexane solution of triisobutylaluminium (TiBA), 0.96 mol/L and 1.84 ml of hexane. The mixture was allowed to react for 2.5 hours under agitation then dried under vacuum.

- 30 1.51 ml of Ionic Activator A (previously dried by prolonged contact with molecular sieves 4A) was reacted with 0.31 ml. of TiBAO solution in cyclohexane (0.812 mol/L) (molar ratio of TiBAO/activator =2 ; Al/B ratio = 4).

1.82 ml of this solution was slowly impregnated (15 min) to the above TiBA treated silica and manually agitated until no lumps were visible. The solution was held for 30 min.

0.72 ml of Complex A solution in heptane (9.17 % wt) was then slowly added
5 (15 min) and manually agitated until no lumps were visible.. Then solution was held for 60 min. and then the catalyst dried under vacuum.

The resultant catalyst had $[Ti] = 40 \text{ mmol/g}$ and $[Al] = 0.83 \text{ mmol/g}$.

Example 2

Polymerisation Data

10 200g PE pellets as bed

Temperature = 70°C

Pressure C2 = 6.5 bars

Pressure ratio C6/C2 = constant at 3010^{-4}

Scavenger = SiO_2/TEA

15 50 ml hydrogen added during phase composition

Polymerisation time = 60 min

Quantity of catalyst injected = 0.092 g

At the end of the polymerisation the polymer produced was separated from the polymer bed by sieving.

20 37.3 g of polymer was produced with activity of 63 g/ghbar.

The supported catalyst of the present invention showed a low decay activity profile with the activity after one polymerisation run of 50 g/ghb.

Example 3

Catalyst preparation

25 To 3g. of Ineos ES70 silica (previously calcined at 500°C for 5 hours under nitrogen, pore volume 1.55 ml/g) was added a solution made with 2.81 ml of a hexane solution of triisobutylaluminium (TiBA), 0.96 mol/L and 1.84 ml of hexane. The mixture was allowed to react for 2.5 hours under agitation then dried under vacuum.

30 1.51 ml of Ionic Activator A (previously dried by prolonged contact with molecular sieves 4A) was reacted with 0.31 ml. of TiBAO solution in cyclohexane (0.812 mol/L) (molar ratio of TiBAO/activator =2 ; Al/B ratio = 4).

1.82 ml of this solution was slowly impregnated (15 min) to the above TiBA

treated silica and manually agitated until no lumps were visible. The solution was held for 30 min.

0.72 ml of Complex A solution in heptane (9.17 % wt) was then slowly added (15 min) and manually agitated until no lumps were visible.. Then solution was held for 5 60 min. and then the catalyst dried under vacuum.

To 1 g. of this catalyst was added 2.5 ml hexane followed by holding for 45 min. after which the catalyst was dried under vacuum.

Example 4

Polymerisation Data

10 200g PE pellets as bed

Temperature = 70°C

Pressure C2 = 6.5 bars

Pressure ratio C6/C2 = constant at 2810^{-4}

Scavenger = SiO₂/TEA

15 40 ml hydrogen added during ghase composition

Polymerisation time = 60 min

Quantity of catalyst injected = 0.093 g

At the end of the polymerisation the polymer produced was separated from the polymer bed by sieving. 39.1 g of polymer was produced with activity of 60 g/ghbar.

20 The polymer had the following properties:

MI (2.16) = 1g/10 min.

Density = 0.921 g/ml

Melt strength (16 Mpa) = 5.9 cN

The supported catalyst of the present invention showed a low decay activity

25 profile with the activity after one polymerisation run of 40 g/ghb. A low exotherm (56°C/g catalyst) was observed compared with a typical temperature in the region of 150°C/g catalyst for prior art catalysts.

Claims:

1. A method for the preparation of a supported metallocene catalyst system said method comprising the steps of:

- (i) mixing together in a suitable solvent
 - (a) aluminoxane and
 - (b) an ionic activator comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen,
- (ii) addition of the mixture from step (i) to a support material, and
- (iii) addition of a metallocene complex in a suitable solvent.

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ABSTRACT
SUPPORTED POLYMERISATION CATALYST

A method for the preparation of a supported metallocene catalyst system comprises the steps of:

- (i) mixing together in a suitable solvent
 - (a) aluminoxane and
 - (b) an ionic activator comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen,
- (iii) addition of the mixture from step (i) to a support material, and
- (iii) addition of a metallocene complex in a suitable solvent.

The use of tetraisobutylaluminoxane results in a more stable activity profile and improved polymer properties in particular melt strength.

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